

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



05 OCT 2004



(43) International Publication Date
8 July 2004 (08.07.2004)

PCT

(10) International Publication Number
WO 2004/056838 A1

(51) International Patent Classification⁷: **C07F 7/18, 7/08**

(21) International Application Number:
PCT/EP2003/015003

(22) International Filing Date: 8 December 2003 (08.12.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02258930.3 20 December 2002 (20.12.2002) EP
03011673.5 23 May 2003 (23.05.2003) EP

(71) Applicant (for all designated States except US): **SIGMA COATINGS B.V.** [NL/NL]; Amsterdamseweg 14, NL-1422 Uithoorn (NL).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **PLEHIERS, Mark** [BE/BE]; Rue Le Corregge, 21, B-1000 Bruxelles (BE).

(74) Agents: **WALSH, David, Patrick** et al.; Appleyards Lees, 15 Clare Road, Halifax HX1 2HY (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

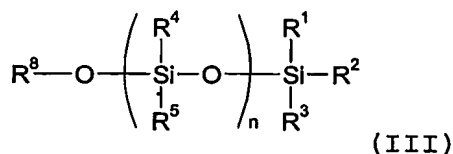
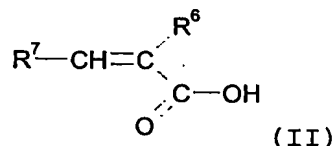
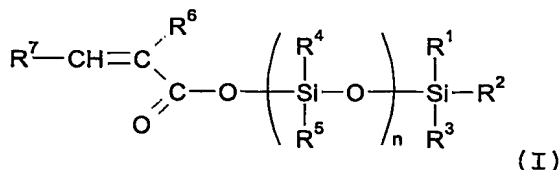
(84) Designated States (regional): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PRODUCTION OF SILYL CARBOXYLATE MONOMERS



(57) Abstract: A process for the production of hydrocarbyl silyl unsaturated carboxylates of formula (I) is described, wherein n represents a number of dihydrocarbylsiloxane units from 0 to 1000. The process includes the reaction of an unsaturated carboxylic acid of formula (II) with a hydrocarbyl silyl compound of formula (III) the said reaction being carried out in the presence of a silaphilic catalyst.



WO 2004/056838 A1

PROCESS FOR THE PRODUCTION OF SILYL CARBOXYLATE MONOMERS

5 The present invention relates to the production of silyl carboxylate by a surprising new route.

Silyl carboxylates are useful as monomers or co-monomers in the production of metal-free binders for self polishing
10 antifouling paints as, for instance, disclosed in EP-A-1127902. Antifouling paints are widely used to improve the performance of ships by preventing the growth of marine organisms on the sub-marine parts of ship's hulls. Binders containing metals such as tin have been widely
15 used since the 1960's but research has shown that the organotin tributyl tin (TBT) causes environmental problems such as deformations in oysters and sex changes in whelks. Silyl carboxylates derived binders are an important replacement for such tin-based systems. Accordingly, the
20 economic production of silyl carboxylate monomers will make an important contribution to such systems.

Some of the polymers used in the above-described antifouling paints are based on silylated carboxylate
25 monomers.

Several processes are known as conventional techniques for the synthesis of said silylated carboxylate monomers.

30 EP 1260513 relates to a process for the preparation of trialkylsilylated carboxylate monomers from hexaalkyldisilylsulfates and metallic salts of unsaturated carboxylic acids.

35 US 6,498,264 discloses the reaction of chlorosilanes having bulky substituent groups with unsaturated acids to produce silyl esters.

JP 5306290 A describes a process to obtain a methacrylic functional group-containing organosilicon compound. The process comprises reacting methacrylic acid with a halogenoalkylsilane (e.g. trialkylsilylchloride) in the presence of a tertiary amine compound having a cyclic structure. This process has disadvantages such as the reduced availability and storage stability of the silyl chloride. Moreover, the reaction yields as a by-product a hydrogen halide (which provokes the corrosion of the production equipment) or a halide salt (which has to be removed by filtration).

The synthesis of trimethylsilyl methacrylate from methacrylic acid and hexamethyldisilazane is described in A.Chapman & A.D.Jenkins J.Polym.Sci. Polym.Chem.Edn. vol 15, p.3075 (1977).

JP 10195084 A discloses the reaction of unsaturated carboxylic acid such as acrylic acid or methacrylic acid with a trialkylsilylhydride compound in the presence of a copper catalyst. One of the disadvantages of this method is the risk of hydrogenation of the unsaturated carboxylic acid due to a side reaction of the produced H₂ on the carbon-carbon double bond.

Reaction mechanisms of nucleophilic attack at silicon have been disclosed in the literature. Bassindale et al, The Chemistry of Organic Silicon Compounds, chapter 13, J Wiley & Sons 1989, discloses extensive reaction mechanisms for silicon. However, the nucleophilic reaction mechanisms relate to halo substituted silicon type compounds and these are encouraged by the halogen leaving group.

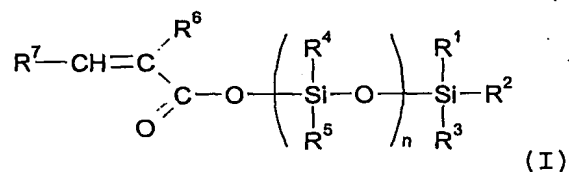
EP 056108A1 (Dow Corning Corporation) discloses the acid catalysed reaction of alkoxysilanes with carboxylic acids to produce alkyl carboxylates and disiloxanes.

5 Nakao et al, Bulletin of the Chemical Society Japan, 54, 1267-1268 (1981) discloses the esterification of carboxylic acids with alcohols in the presence of trimethyl chlorosilane. The reaction is said to proceed via the intermediate alkoxy trimethyl silane and produces
10 the alkyl ester in high yield together with disiloxane. The yields of methyl acetate are 96-98%.

It is one of the objects of the present invention to
15 provide a process for the production of silyl carboxylates.

It is a further object of the present invention to provide a more convenient and efficient process for the production
20 of silyl carboxylates.

According to a first aspect of the present invention there is provided a process for the production of hydrocarbyl silyl unsaturated carboxylates of formula (I).
25



wherein

30 $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5$ each independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxy, aralkyloxy, $-\text{O}-\text{SiR}^1\text{R}^2\text{R}^3$, $-\text{O}-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ or aralkyl radical optionally substituted by one or more substituents independently selected from the group

comprising alkyl, alkoxy, aralkyl, aralkyloxy, aryl, aryloxy, silyl, $-O-SiR^1R^2R^3$, $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$, hydroxyl, halogen, amino or amino alkyl radicals, or may independently be an $-O-C(O)-C(R^6)=CHR^7$ group;

5

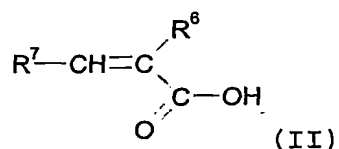
R⁶ represents a hydrogen atom, or an alkyl group, or (-R¹¹-)_n. C(O)OR¹⁰ wherein R¹⁰ represents an hydrogen atom, -(SiR⁴R⁵O)_n-SiR¹R²R³ wherein R¹, R², R³, R⁴, R⁵ are as already defined or an alkyl group; wherein R¹¹ is independently selected from alkyl, alkenyl, alkynyl, aryl or an aralkyl radical optionally substituted by one or more substituents independently selected from alkyl, alkenyl, alkynyl, aralkyl, aryl, hydroxyl, halogen, amino or amino alkyl radicals; O=0 or 1;

15

R⁷ represents a hydrogen atom, or independently represents alkyl, aryl, aralkyl, alkenyl, alkynyl radical optionally substituted with the same radicals as defined for R⁶ above or R⁷ represents -COOR⁹ wherein R⁹ represents an hydrogen atom, an alkyl group or -(SiR⁴R⁵-O)_n- SiR¹R²R³ wherein R¹, R², R³, R⁴ and R⁵ are as already defined;

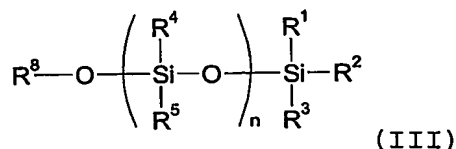
by reaction of an unsaturated carboxylic acid of formula
(II)

25



wherein R⁶ and R⁷ in formula (II) are as defined above;
with a hydrocarbonyl silyl compound of formula (III)

30



wherein $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ and R^5 are as defined above and R^8 is an hydrogen atom, an alkyl, aralkyl or aryl, alkenyl or alkynyl group optionally substituted with one or more substituents selected from the equivalent substituents as detailed for R^1-R^5 above; and each n above independently represents a number of dihydrocarbylsiloxane units from 0 to 1000; the said reaction being carried out in the presence of a silaphilic catalyst.

Preferably, wherein when R^{10} represents alkyl or hydrogen in formula II, it represents $-(\text{SiR}^4\text{R}^5\text{O})_n\text{SiR}^1\text{R}^2\text{R}^3$ in formula I, wherein n and R^1-R^5 are as defined previously.

Preferably, wherein when $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ or R^5 are aryloxyl, alkaryloxyl, alkoxy or hydroxyl in formula III, they may represent $-\text{O}-\text{C}(\text{O})-\text{C}(\text{R}^6)=\text{CHR}^7$ in formula I.

Preferably, where R^9 represents an alkyl group or an hydrogen atom in formula (II), it may represent $-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ in formula (I).

Preferably, the silaphilic catalysts are selected from fluoride containing mineral or organic salts which comprise, but are not limited to, sodium fluoride, potassium fluoride, caesium fluoride or tetrabutyl ammonium fluoride (Bu_4NF); or are selected from N-methyl imidazole (NMI), N,N-dimethylamino pyridine (DMAP), hexamethylphosphoric triamide (HMPA), 4,4 dimethyl imidazole, N-methyl-2-pyridone (NMP), pyridine N-oxide, triphenylphosphine oxide, 2,4 dimethyl pyridine, N-methyl-4-pyridone, dimethyl formamide (DMF), 3,5 dimethyl pyridine, N,N-dimethylethylene Urea (DMEU), N,N-

dimethylpropylene Urea(DMPU), pyridine, imidazole, trimethylamine, dimethyl sulphoxide(DMSO), N-methyl pyrrolidinone(NMP), formamide, N-alkylformamides, N,N-dialkylformamides, acetamide, N-alkylacetamides, N,N-dialkylacetamides, alkylcyanides, N-methyl pyrrolidone, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole, LiOH, LiStearate, NaI, MeONa or MeOLi; the term alkyl in the above N-alkyl and N,N-dialkyl . . . amides and cyanides include any linear, cyclic, bicyclic, polycyclic, alkyl aliphatic or aromatic group and in the case of N,N-compounds the alkyl may be the same or different, an example is N-formyl Rosinamine.

Silaphilic catalysts have been defined as molecules having a special affinity for silicon - Brook, Silicon in Organic, Organometallic and Polymer Chemistry section 5.5, J Wiley & Sons 2000. Preferably, the silaphilic catalysts have an electron rich heteroatom such as oxygen or nitrogen. Typically, the hetero atom is substituted with electron donating groups.

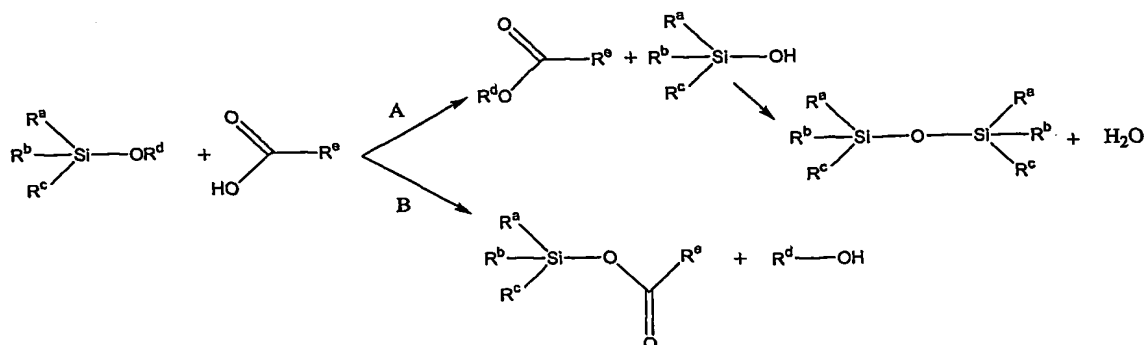
Lewis acid catalysts may also be used to catalyse the process of the present invention. Accordingly, for the purposes of the present invention, the term "silaphilic catalyst" should be taken as incorporating Lewis acid catalysts such as titanium butoxide $Ti(OBu)_4$.

Said catalyst may, for example, be a metal alkoxide, an organic tin compound such as dibutyltin dilaurate, dibutyltin dioctate or dibutyltin diacetate, or a boron compound such as boron butoxide or boric acid. Illustrative examples of metal alkoxide include aluminum triethoxide, aluminum triisopropoxide, aluminum tributoxide, aluminum tri-sec-butoxide, aluminum diisopropoxy-sec-butoxide, aluminum diisopropoxyacetyl acetate, aluminum di-sec-butoxyacetyl acetate, aluminum diisopropoxyethyl acetoacetate, aluminum di-sec-

butoxyethylacetoacetate, aluminum trisacetyl acetate, aluminum trisethylaceto acetate, aluminum acetylacetate bisethylacetoacetate, titanium tetraethoxide, titanium tetraisopropoxide, titanium (IV) butoxide, titanium diisopropoxybisacetyl acetate, titanium diisopropoxybisethyl acetoacetate, titanium tetra-2-ethylhexyloxide, titanium diisopropoxybis(2-ethyl-1,3-hexanediolate), titanium dibutoxybis(triethanolaminate), zirconium tetrabutoxide, zirconium tetraisopropoxide, zirconium tetramethoxide, zirconium tributoxide monoacetylacetate, zirconium dibutoxide bisacetylacetate, zirconium butoxide trisacetylacetate, zirconium tetraacetylacetate, zirconium tributoxide monoethylacetoacetate, zirconium dibutoxide bisethylacetoacetate, zirconium butoxide trisethylacetoacetate and zirconium tetraethylacetoacetate. In addition to these compounds, cyclic 1,3,5-triisopropoxycyclotrialuminoxane and the like can also be used and is thereby incorporated within the definition of "silaphilic catalyst".

Preferably, in compounds of formula I, the number of (alk)acryloyl groups is less than 4, more preferably, less than 3, most preferably 1.

Advantageously, although the prior art describes the reaction of alkoxysilanes with carboxylic acid as leading to the corresponding alkylcarboxylates and the silanol (path A), the latter tending to dehydrate to form disiloxanes. It has been surprisingly discovered that the use of a silaphilic catalyst (ie. a catalyst able to coordinate in a reversible manner with the silicon atom) allows preferential substitution of alkoxy or hydroxyl groups by the carboxy group (path B).



Advantageously, the process of the present invention
 5 results in the release of harmless by-products, namely
 water and methanol.

More preferably, the silaphilic catalyst is a catalyst
 capable of facilitating a penta or hexa coordinated
 10 silicon species in the transition state of the reaction.

More, preferably, the silaphilic catalysts are
 independably selected from

15 DMF, DMSO, formamide, N-alkylformamides, N,N-
 dialkylformamides, acetamide, N-alkylacetamides, N,N-
 dialkylacetamides, N-Methyl pyrrolidone, p-
 dimethylaminobenzaldehyde, DMAP, N-methyl imidazole, 1,2-
 dimethyl imidazole, HMPA, DMPU, NaI, MeONa, MeOLi, Bu₄NF,
 20 Ph₃PO, LiOH, LiStearate and pyridine N-oxide.

The catalysts may be homogenous or heterogenous but
 preferably, are homogenous and present in a free form in
 the reaction medium. Alternatively, the catalysts may be
 25 bonded to a polymeric support.

Particularly preferred catalysts are independably selected
 from

DMF, formamide, N-alkyl formamide, N,N-dialkylformamide, Bu₄NF.

5 Preferably, the catalysts are present at a level of 0.001-100 mol% (mol/mol silane), more preferably 0.01-40 mol%, most preferably, 0.1-30 mol% in the reaction medium at the start of the reaction. Especially preferred is a range of 20-30 mol% for the formamides or 0.1-1mol% for Bu₄NF.

10

Preferably, the reaction includes a polymeric inhibitor. A suitable polymerisation inhibitor is o-methoxyphenol.

15 Preferably, the reaction is carried out in a suitable solvent.

Suitable solvents which can be used in the process of the invention include non polar inert solvents, aliphatic hydrocarbons, cyclic and non cyclic ethers.

20

Suitable solvents may be independently selected from pentane, hexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthlene, diethyl ether, diisopropyl ether, 25 diisobutyl ether or mixtures thereof.

Especially preferred solvents are those which allow reactive distillation ie. which cause no distillation of any of the reactants but which allow preferential 30 distillation of one of the products to drive the equilibrium to the right.

More especially preferred solvents are those which form a low boiling azeotrope with the distilled R⁸OH. Still more 35 especially preferred solvents are those which form a heterogenous low boiling azeotrope with the distilled R⁸OH.

Most preferably, the solvents are independently selected from pentane, hexane, heptane, toluene and xylene.

5 Preferably, the temperature of the reaction depends on the boiling point of the azeotrope that has to be distilled, the shape of the reactor and the height of the distillation column.

10 Typically, the reaction is carried out in the range 0°C - 200°C, more preferably, 60-170°C, most preferably, 110-140°C.

15 Preferably, the polymerisation inhibitor is present in the range 0.001-10% wt/wt of the total reaction mix, more preferably 0.001-5% wt/wt and most preferably 0.01-2% wt/wt.

20 Preferably, the molar ratio of silane:acid is between 1:100 and 50:1, more preferably between 10:1 and 1:10, most preferably, between 2:1 and 1:2. Preferably, the molar ratio of silane:acid is approximately 1:1.

25 Preferably, the solvent is at least 10 wt% of the total reaction mix at the start of the reaction, more preferably, at least 20 wt%, most preferably, at least 30 wt%. The reaction may be carried out at atmospheric pressure although both higher and lower pressures are also possible.

30 The reaction may also be performed without solvent and accordingly suitable ranges of solvent are 0-99 wt% of the total reaction mix, more preferably, 20-50 wt%, most preferably 30-40 wt%.

35 Preferably, R¹, R², R³, R⁴ and R⁵ each independently represent hydrogen, alkyl, alkynyl, aryl or aralkyl radicals optionally substituted as aforesaid in the first

aspect of the present invention, more preferably, optionally substituted by one or more substituents independently selected from the group comprising alkyl, aralkyl, aryl, silyl, halogen, tertiary amino or amino
5 alkyl radicals.

Preferably, R^6 represents an hydrogen atom or an alkyl group.

10 Preferably, R^7 represents an alkyl group, an aryl group or an aralkyl group.

Preferably, R^1 , R^2 , R^3 , R^4 , R^5 each independently represent an alkyl, an aryl group or a hydrogen atom.

15

According to an embodiment of the present invention, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 and R^9 are each independently selected from the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl.

20 Preferably, R^4 , R^5 , R^6 and R^9 are methyl and R^7 is hydrogen.

Preferably, R^8 represents a hydrogen atom or an alkyl group.

25 When R^1 , R^2 and R^3 are alkyl groups they are preferably, independently selected from the group consisting of C1 to C8 alkyl groups, preferably C3 and C4, more preferably isopropyl and n-butyl. The said alkyl groups may be branched or linear and, optionally, they may be
30 substituted as aforesaid in the first aspect.

Preferably, when any one of R^1 - R^5 is selected as $-O-SiR^1R^2R^3$ or $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$ the R^1 - R^5 groups attached to the silicon radical in the selected group are not themselves,
35 $-O-SiR^1R^2R^3$ or $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$. Preferably, when any one of the R^1 - R^5 groups is selected as $-O-SiR^1R^2R^3$ or $-O-(SiR^4R^5O)_n-SiR^1R^2R^3$ and such groups are substituted, the

substitution is at the R^1 - R^5 groups and is preferably, by alkyl, alkoxy, aralkyl, aralkyloxy, hydroxy, aryl, aryloxy, silyl, halogen, amino or amino alkyl, more preferably, alkyl or aryl, most preferably, alkyl.

5

Preferably, each n in formulas I, II or III is independently 0 to 50, more preferably, 0 to 10, most preferably 0 to 5. Especially preferred values for n are selected from 0, 1, 2, 3, 4 or 5.

10

As used herein, the term "polymer" refers to the product of a polymerisation reaction, and is inclusive of homopolymers, copolymers, terpolymers, etc.

15 As used herein, the term "copolymer" refers to polymers formed by the polymerisation reaction of at least two different monomers.

20 As used herein, the term "independently selected" or "independently represent" indicates that each radical R so described, can be identical or different. For example each R^i in compound of formula (I) may be different for each value of n .

25 The term "alkyl", as used herein unless otherwise defined, relates to saturated hydrocarbon radicals having straight, branched, cyclic or polycyclic moieties or combinations thereof and contains 1 to 20 carbon atoms, preferably 1 to 10 carbon atoms, more preferably 1 to 8 carbon atoms, 30 still more preferably 1 to 6 carbon atoms, yet more preferably 1 to 4 carbon atoms. Examples of such radicals include may be independently selected from methyl, ethyl, n -propyl, isopropyl n -butyl, isobutyl, set-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl, 35 3-methylpentyl, octyl and the like.

The term "alkenyl", as used herein, relates to hydrocarbon radicals having one or several double bonds, having straight, branched, cyclic or polycyclic moieties or combinations thereof and containing from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkenyl groups include vinyl, allyl, isopropenyl, pentenyl, hexenyl, heptenyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, 1-propenyl, 2-butenyl, 2-methyl-2-butenyl, isoprenyl, farnesyl, geranyl, geranylgeranyl and the like.

The term "alkynyl", as used herein, relates to hydrocarbon radicals having one or several triple bonds, having straight, branched, cyclic or polycyclic moieties or combinations thereof and having from 2 to 18 carbon atoms, preferably 2 to 10 carbon atoms, more preferably from 2 to 8 carbon atoms, still more preferably from 2 to 6 carbon atoms, yet more preferably 2 to 4 carbon atoms. Examples of alkynyl radicals include ethynyl, propynyl, (propargyl), butynyl, pentynyl, hexynyl and the like.

The term "aryl" as used herein, relates to an organic radical derived from an aromatic hydrocarbon by removal of one hydrogen, and includes any monocyclic, bicyclic or polycyclic carbon ring of up to 7 members in each ring, wherein at least one ring is aromatic. Said radical may be optionally substituted with one or more substituents independently selected from alkyl, alkoxy, halogen, hydroxy or amino radicals. Examples of aryl includes phenyl, p-tolyl, 4-methoxyphenyl, 4-(tert-butoxy)phenyl, 3-methyl-4-methoxyphenyl, 4-fluorophenyl, 4-chlorophenyl, 3-nitrophenyl, 3-aminophenyl, 3-acetamidophenyl, 4-acetamidophenyl, 2-methyl-3-acetamidophenyl, 2-methyl-3-aminophenyl, 3-methyl-4-aminophenyl, 2-amino-3-methylphenyl, 2,4-dimethyl-3-aminophenyl, 4-hydroxyphenyl,

3-methyl-4-hydroxyphenyl, 1-naphthyl, 2-naphthyl, 3-amino-1-naphthyl, 2-methyl-3-amino-1-naphthyl, 6-amino-2-naphthyl, 4,6-dimethoxy-2-naphthyl, tetrahydronaphthyl, indanyl, biphenyl, phenanthryl, anthryl or acenaphthyl and
5 the like.

The term "aralkyl" as used herein, relates to a group of the formula alkyl-aryl, in which alkyl and aryl have the same meaning as defined above. Examples of aralkyl
10 radicals include benzyl, phenethyl, dibenzylmethyl, methylphenylmethyl, 3- (2-naphthyl)-butyl, and the like.

The term "silyl" as used herein includes $-\text{SiR}^1\text{R}^2\text{R}^3$ and $-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ groups wherein R^1-R^5 are as defined
15 herein. Preferably when the $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ or R^5 group in formula (I) is substituted by such a silyl group at least one or more of $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ and R^5 in the silyl group $-\text{SiR}^1\text{R}^2\text{R}^3$ or $-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ are alkyl or aryl and at least one or more of $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ and R^5 in the said silyl
20 group which are not alkyl or aryl are $-\text{O}-\text{SiR}^1\text{R}^2\text{R}^3$ or $-\text{O}-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$.

In the silyl $-\text{SiR}^1\text{R}^2\text{R}^3$ or $-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$, if R^1 is alkyl or aryl and at least one of R^2 and R^3 is $-\text{O}-\text{SiR}^1\text{R}^2\text{R}^3$
25 or $-\text{O}-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ then, preferably, $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ and R^5 in such $-\text{O}-\text{SiR}^1\text{R}^2\text{R}^3$ or $-\text{O}-(\text{SiR}^4\text{R}^5\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ groups are themselves alkyl or aryl and may be the same or different, more preferably, each independently may be $\text{C}_1 - \text{C}_8$ alkyl groups.

30 Examples of the ethylenically unsaturated part of formula (I) may include but are not limited to (meth)acrylate, itaconate, methyl fumarate, methyl maleate, n-butyl fumarate, n-butyl maleate, amyl fumarate, amyl maleate,
35 and the like and polymers or copolymers thereof, wherein methacrylate or acrylate is herein collectively referred to as a "(meth)acrylate".

In a preferred embodiment, said ethylenically unsaturated part of formula (I) is (meth)acrylate, and copolymers or polymers thereof.

5 Examples of the organosilylated carboxylate monomers of general formula (I) include but are not limited to tri-n-butyl 1-(meth)acryloyloxy-silane, tri-n-propyl-1-(meth)acryloyloxy silane, tri-t-butyl-1-(meth)acryloyloxy-silane, tri-isopropyl-1-(meth)acryloyloxy-silane, tri-isobutyl-1-(meth)acryloyloxy-silane, tri-methyl-1-(meth)acryloyloxy-silane, triethyl- 1-(meth)acryloyloxy-silane, tribenzyl- 1-(meth)acryloyloxy-silane, triamyl- 1-(meth)acryloyloxy-silane, triphenyl- 1-(meth)acryloyloxy-silane, nonamethyl-1-(meth)acryloyloxy-tetrasiloxane, nonaethyl-1-(meth)acryloyloxy-tetrasiloxane, nona-t-butyl-1-(meth)acryloyloxy-tetrasiloxane, nonabenzyl-1-(meth)acryloyloxy-tetrasiloxane, nona-isopropyl-1-(meth)acryloyloxy-tetrasiloxane, nona-n-propyl-1-(meth)acryloyloxy-tetrasiloxane, nona-isobutyl-1-(meth)acryloyloxy-tetrasiloxane, nona-amyl-1-(meth)acryloyloxy-tetrasiloxane, nona-n-butyl-1-(meth)acryloyloxy-tetrasiloxane, nona-dodecyl-1-(meth)acryloyloxy-tetrasiloxane, nona-hexyl-1-(meth)acryloyloxy-tetrasiloxane, nona-phenyl-1-(meth)acryloyloxy-tetrasiloxane, nona-octyl-1-(meth)acryloyloxy-tetrasiloxane, undecamethyl-1-(meth)acryloyloxy-pentasiloxane, undecaethyl-1-(meth)acryloyloxy-pentasiloxane, undeca-t-butyl-1-(meth)acryloyloxy-pentasiloxane, undecabenzyl-1-(meth)acryloyloxy-pentasiloxane, undeca-isopropyl-1-(meth)acryloyloxy-pentasiloxane, undeca-n-propyl-1-(meth)acryloyloxy-pentasiloxane, undeca-isobutyl-1-(meth)acryloyloxy-pentasiloxane, undeca-amyl-1-(meth)acryloyloxy-pentasiloxane, undeca-n-butyl-1-(meth)acryloyloxy-pentasiloxane, undeca-dodecyl-1-(meth)acryloyloxy-pentasiloxane, undeca-hexyl-1-

- | | | |
|----|---|------------------------|
| | (meth) acryloyloxy-pentasiloxane, | undeca-phenyl-1- |
| | (meth) acryloyloxy-pentasiloxane, | undeca-octyl-1- |
| | (meth) acryloyloxy-pentasiloxane | tridecamethyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | tridecaethyl-1- |
| 5 | (meth) acryloyloxy-hexasiloxane, | trideca-t-butyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | tridecabenzyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-isopropyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-n-propyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-isobutyl-1- |
| 10 | (meth) acryloyloxy-hexasiloxane, | trideca-amyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-n-butyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-dodecyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-hexyl-1- |
| | (meth) acryloyloxy-hexasiloxane, | trideca-phenyl-1- |
| 15 | (meth) acryloyloxy-hexasiloxane, | trideca-octyl-1- |
| | (meth) acryloyloxy-hexasiloxane | 1,3,3,3-tetramethyl-1- |
| | trimethylsilyloxy-1- (meth) acryloyloxy-disiloxane, | |
| | 1-ethyl,3,3,3-trimethyl-1-trimethylsilyloxy-1- | |
| | (meth) acryloyloxy-disiloxane, | |
| 20 | tris- (trimethylsilyloxy) -1-methacryloyloxy-silane | and |
| | polymers thereof. | |

In formula I, the ethylenic unsaturated part is most preferably selected from acrylate and methacrylate.

25

The invention will now be described by way of illustration only and with reference to the accompanying examples.

In the following examples, NMR data has been determined in CDCl₃ and are expressed as delta versus TMS.

30

Example 1:

A mixture of 20 g of methoxytributyl silane (CAS RN:15811-64-0), 8.12 g of methacrylic acid, 1.89 g of N,N-dimethylformamide, 0.2 g of p-methoxyphenol and 30 ml of heptane is heated until methanol is completely distilled

35

at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate (89%).

Tri-n-butylsilyl methacrylate: ^{13}C NMR : 167.8, 137.9, 126.0, 26.7, 25.5, 18.5, 13.5, 14.0; ^{29}Si NMR : 23.1; IR (film): 2959, 2927, 1703, 1334, 1174, 886, 766 cm^{-1} .

Example 2:

A mixture of 10 g of tributyl silanol (CAS RN: 18388-85-7), 4.26 g of methacrylic acid, 0.94 g of N,N-dimethylformamide, 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until water is completely distilled at atmospheric pressure (b.p. of the azeotrope: 79.2°C) to furnish tributylsilyl methacrylate.

Comparative Example:

A mixture of 10 g of methoxytributyl silane, 4.26 g of methacrylic acid, 1.3 g of Amberlyst A15 (sulfonic acid resin), 0.1 g of p-methoxyphenol and 10 ml of heptane is heated. After distillation of heptane, only slight amounts of tributylsilyl methacrylate are detected, hexabutyl disiloxane and methyl methacrylate are present as main products.

Example 3:

A mixture of 10 g of tributyl silanol, 4.26 g of methacrylic acid, 0.58 g of formamide, 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until water is completely distilled at atmospheric pressure (b.p. of the azeotrope: 79.2°C) to furnish tributylsilyl methacrylate.

Example 4:

A mixture of 10 g of methoxytributyl silane, 4.26 g of methacrylic acid, 1.13 g of N,N-dimethyl acetamide, 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until

methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate.

5 Example 5:

A mixture of 10 g of methoxytributyl silane, 4.26 g of methacrylic acid, 2.0 g of N-formyl Rosinamine (prepared as described in example 1 of WO00/55117) , 0.1 g of p-methoxyphenol and 10 ml of heptane is heated until
10 methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate.

Example 6

15 0.274 g of tetrabutylammonium fluoride trihydrate and 30 ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 20 g of methoxytributyl silane, 8.12 g of methacrylic acid and 0.2 g of p-methoxyphenol were then added. The mixture was heated
20 until methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) for 2 h. Evaporation of the solvent under reduced pressure followed by vacuum distillation furnished pure tributylsilyl methacrylate.

25

Example 7

0.179 g of tetrabutylammonium fluoride trihydrate and 20ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 10 g of triisopropylsilanol,
30 4.41 g of acrylic acid and 0.2 g of p-methoxyphenol were then added. The mixture was heated until the water is totally distilled at atmospheric pressure (b.p. of the azeotrope: 79.2°C) to furnish triisopropyl acrylate.

Triisopropylsilyl acrylate: ¹³C NMR: 132.5, 130.4, 175.0,
35 12.3, 17.0; ²⁹Si NMR: 21.84; IR (film): 2948, 2870, 1708, 1620, 1465, 1403, 1290, 1209, 1046, 884, 818, 746 cm⁻¹.

Example 8

0.132 g of tetrabutylammonium fluoride trihydrate and 20ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 13.8 g of nonamethyl-1-methoxy-tetrasiloxane (CAS: 78824-97-2), 4.41 g of methacrylic acid and 0.1 g of p-methoxyphenol were then added. The mixture was heated until the methanol is totally distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish nonamethyl-1-methacryloyloxy-tetrasiloxane.

Nonamethyl-1-methacryloyloxy-tetrasiloxane: ^{13}C NMR: 166.8, 126.3, 137.8, 18.1, 1.95, 1.24, 1.03, -0.13; ^{29}Si NMR: 7.3, -8.8, -20.1, -21.6; IR (film): 2963, 1730, 1372, 1260, 1083, 1045, 841, 809 cm^{-1} .

Comparative example 2 shows the behaviour of an uncatalysed reaction, the reaction is very slow and leads to a mixture of starting materials and MMA.

Comparative example 2

A mixture of 20 g of methoxytributyl silane, 8.12 g of methacrylic acid, 0.2 g of p-methoxyphenol and 30 ml of heptane is heated. After 7 h at 165 °C only 0.15 eq. of methanol was distilled. Analysis of the reaction mixture by GC showed a mixture of starting materials, TBSiMA and methyl methacrylate.

Example 9:

0.36 g of lithium hydroxide monohydrate and 20ml of heptane were heated at 110°C in order to remove water by azeotropic distillation. 20 g of methoxytributylsilane, 8.12 g of methacrylic acid and 0.2 g of p-methoxyphenol were then added. The mixture was heated is heated until the methanol is totally distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish tributylsilyl methacrylate (88%).

Example 10:

A mixture of 21.9 g of 1,1,1,3,5,5,5-heptamethyl-3-methoxytrisiloxane (CAS RN:7671-19-4), 8.12 g of
5 methacrylic acid, 1.89 g of N,N-dimethylformamide, 0.2 g of p-methoxyphenol and 30 ml of heptane is heated until methanol is completely distilled at atmospheric pressure (b.p. of the azeotrope: 59.1°C) to furnish 1,3,3,3-tetramethyl-1-trimethylsilyloxy-1-(meth)acryloyloxy-
10 disiloxane.

1,3,3,3-tetramethyl-1-trimethylsilyloxy-1-(meth)acryloyloxy-disiloxane: ^{13}C NMR : 166.4, 137.7, 126.30, 18.5, 1.7, -2.7; ^{29}Si NMR : 10.1, -57.8; IR (film): 2962, 1708, 1453, 1336, 1312, 1256, 1184, 1090,
15 1009, 953, 846, 800, 758 cm^{-1} .

The reaction temperatures for the above mentioned examples are as follows:-

20	Example #	T°
	1	150-170°C
	2	120-130°C
	3	120-140°C
	4	130-150°C
25	5	125-130°C
	6	110-120°C
	7	125-130°C
	8	110-135°C
	9	125-150°C
30	10	150-170°C

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to
35 this specification in connection with this application and which are open to public inspection with this specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

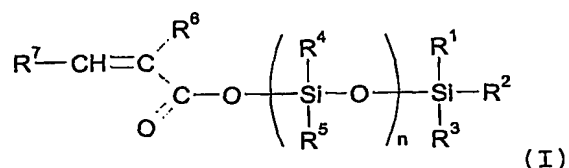
15

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

20

Claims

1. A process for the production of hydrocarbyl silyl
5 unsaturated carboxylates of formula (I).



wherein

10

R^1 , R^2 , R^3 , R^4 , R^5 each independently represent hydrogen, hydroxyl, alkyl, alkenyl, alkynyl, alkoxyl, aryl, aryloxy, aralkyloxy, $\text{---O---SiR}^1\text{R}^2\text{R}^3$, $\text{---O---(SiR}^4\text{R}^5\text{O)}_n\text{---SiR}^1\text{R}^2\text{R}^3$ or aralkyl radical optionally substituted by one or more
15 substituents independently selected from the group comprising alkyl, alkoxyl, aralkyl, aralkyloxy, aryl, aryloxy, silyl, $\text{---O---SiR}^1\text{R}^2\text{R}^3$, $\text{---O---(SiR}^4\text{R}^5\text{O)}_n\text{---SiR}^1\text{R}^2\text{R}^3$, hydroxyl, halogen, amino or amino alkyl radicals, or may independently be an $\text{---O---C(O)---C(R}^6\text{)=CHR}^7$ group;

20

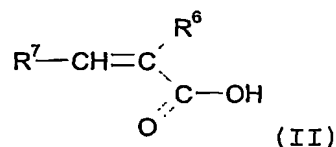
R^6 represents a hydrogen atom, or an alkyl group, or $(\text{---R}^{11}\text{---})_0$, C(O)OR^{10} wherein R^{10} represents an hydrogen atom, $\text{---(SiR}^4\text{R}^5\text{O)}_n\text{---SiR}^1\text{R}^2\text{R}^3$ wherein R^1 , R^2 , R^3 , R^4 , R^5 are as already defined or an alkyl group; wherein R^{11} is independently
25 selected from alkyl, alkenyl, alkynyl, aryl or an aralkyl radical optionally substituted by one or more substituents independently selected from alkyl, alkenyl, alkynyl, aralkyl, aryl, hydroxyl, halogen, amino or amino alkyl radicals; $\text{O}=0$ or 1 ;

30

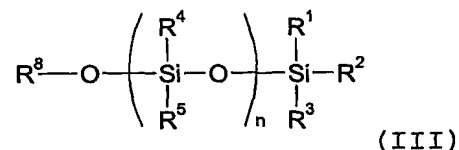
R^7 represents a hydrogen atom, or independently represents alkyl, aryl, aralkyl, alkenyl, alkynyl radical optionally substituted with the same radicals as defined for R^6 above or R^7 represents ---COOR^9 wherein R^9 represents an hydrogen

atom, an alkyl group or $-(\text{SiR}^4\text{R}^5-\text{O})_n-\text{SiR}^1\text{R}^2\text{R}^3$ wherein R^1 , R^2 , R^3 , R^4 and R^5 are as already defined;

by reaction of an unsaturated carboxylic acid of formula
5 (II)



wherein R^6 and R^7 in formula (II) are as defined above;
10 with a hydrocarbyl silyl compound of formula (III)



15 wherein $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ and R^5 are as defined above and R^8 is an hydrogen atom, an alkyl, aralkyl or aryl, alkenyl or alkynyl group optionally substituted with one or more substituents selected from the equivalent substituents as detailed for R^1-R^5 above; and each n above independently
20 represents a number of dihydrocarbylsiloxane units from 0 to 1000; the said reaction being carried out in the presence of a silaphilic catalyst.

2. A process according to claim 1, wherein $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$,
25 R^5 each independently represent an alkyl, an aryl group or a hydrogen atom.

3. A process according to claim 1 or 2, wherein $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6$ and R^9 are each independently selected from
30 the group comprising methyl, ethyl, propyl, isopropyl, isobutyl, n-butyl, sec-butyl, t-butyl.

4. A process according to claims 1, 2 or 3 wherein R⁴, R⁵, R⁶, R⁷ and R⁹ are independently methyl.
5. A process according to claims 1, 2, 3 or 4 wherein R¹, R² and R³ are n-butyl.
6. A process according to any preceding claim, wherein fluoride containing mineral or organic salts which
10 comprise, but are not limited to, sodium fluoride, potassium fluoride, caesium fluoride or tetrabutyl ammonium fluoride (Bu₄NF); or are selected from N-methyl imidazole (NMI), N,N-dimethylamino pyridine (DMAP), hexamethylphosphoric triamide (HMPA), 4,4 dimethyl
15 imidazole, N methyl-2-pyridone (NMP), pyridine N-oxide, triphenylphosphine oxide, 2,4 dimethyl pyridine, N-methyl-4-pyridone, dimethyl formamide (DMF), 3,5 dimethyl pyridine, N,N-dimethylethylene Urea (DMEU), N,N-dimethylpropylene Urea (DMPU), pyridine, imidazole,
20 trimethylamine, dimethyl sulphoxide (DMSO), N-methyl pyrrolidinone (NMP), formamide, N-alkylformamides, N,N-dialkylformamides, acetamide, N-alkylacetamides, N,N-dialkylacetamides, alkylcyanides, N-methyl pyrrolidone, p-dimethylaminobenzaldehyde, 1,2-dimethyl imidazole, LiOH,
25 LiStearate, NaI, MeONa or MeOLi; the term alkyl in the above N-alkyl and N,N-dialkyl amides and cyanides includes any linear, cyclic, bicyclic, polycyclic, alkyl aliphatic or aromatic group and in the case of N,N-compounds the alkyl may be the same or different, an
30 example is N-formyl Rosinamine.
7. A process according to any preceding claim, wherein the catalysts are homogenous or heterogenous.
8. A process according to any preceding claim wherein the
35 catalyst is able to coordinate reversibly with the silicon atom.

9. A process according to claim 8, wherein the catalyst is capable of forming a penta or hexa coordinated silicon species.

5 10. A process according to claim 1, wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^8 , R^9 and R^7 are alkyl radicals independently selected from methyl, ethyl, n-propyl, isopropyl n-butyl, isobutyl, set-butyl, tert-butyl, 2-methylbutyl, pentyl, iso-amyl, hexyl, cyclohexyl, 3-methylpentyl, octyl and the
10 like.

11. A process according to claim 1, wherein the hydrocarbonyl silyl esters of formula I are selected from
15 tri-n-butyl 1-(meth)acryloyloxy-silane, tri-n-propyl-1-(meth)acryloyloxy silane, tri-t-butyl-1-(meth)acryloyloxy-silane, tri-isopropyl-1-(meth)acryloyloxy-silane, tri-isobutyl-1-(meth)acryloyloxy-silane, tri-methyl-1-(meth)acryloyloxy-silane, triethyl- 1-(meth)acryloyloxy-silane, tribenzyl- 1-(meth)acryloyloxy-silane, triamyl- 1-
20 (meth)acryloyloxy-silane, triphenyl- 1-(meth)acryloyloxy-silane, nonamethyl-1-(meth)acryloyloxy-tetrasiloxane, nonaethyl-1-(meth)acryloyloxy-tetrasiloxane, nona-t-butyl-1-(meth)acryloyloxy-tetrasiloxane, nonabenzyl-1-(meth)acryloyloxy-tetrasiloxane,
25 (meth)acryloyloxy-tetrasiloxane, nona-isopropyl-1-(meth)acryloyloxy-tetrasiloxane, nona-n-propyl-1-(meth)acryloyloxy-tetrasiloxane, nona-isobutyl-1-(meth)acryloyloxy-tetrasiloxane, nona-amyl-1-(meth)acryloyloxy-tetrasiloxane, nona-n-butyl-1-(meth)acryloyloxy-tetrasiloxane, nona-dodecyl-1-(meth)acryloyloxy-tetrasiloxane,
30 (meth)acryloyloxy-tetrasiloxane, nona-hexyl-1-(meth)acryloyloxy-tetrasiloxane, nona-phenyl-1-(meth)acryloyloxy-tetrasiloxane, nona-octyl-1-(meth)acryloyloxy-tetrasiloxane, undecamethyl-1-(meth)acryloyloxy-pentasiloxane, undecaethyl-1-(meth)acryloyloxy-pentasiloxane,
35 (meth)acryloyloxy-pentasiloxane, undeca-t-butyl-1-(meth)acryloyloxy-pentasiloxane, undecabenzyl-1-(meth)acryloyloxy-pentasiloxane, undeca-isopropyl-1-

(meth) acryloyloxy-pentasiloxane, undeca-n-propyl-1-
 (meth) acryloyloxy-pentasiloxane, undeca-isobutyl-1-
 (meth) acryloyloxy-pentasiloxane, undeca-amyl-1-
 (meth) acryloyloxy-pentasiloxane, undeca-n-butyl-1-
 5 (meth) acryloyloxy-pentasiloxane, undeca-dodecyl-1-
 (meth) acryloyloxy-pentasiloxane, undeca-hexyl-1-
 (meth) acryloyloxy-pentasiloxane, undeca-phenyl-1-
 (meth) acryloyloxy-pentasiloxane, undeca-octyl-1-
 (meth) acryloyloxy-pentasiloxane, tridecamethyl-1-
 10 (meth) acryloyloxy-hexasiloxane, tridecaethyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-t-butyl-1-
 (meth) acryloyloxy-hexasiloxane, tridecabenzyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-isopropyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-n-propyl-1-
 15 (meth) acryloyloxy-hexasiloxane, trideca-isobutyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-amyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-n-butyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-dodecyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-hexyl-1-
 20 (meth) acryloyloxy-hexasiloxane, trideca-phenyl-1-
 (meth) acryloyloxy-hexasiloxane, trideca-octyl-1-
 (meth) acryloyloxy-hexasiloxane - (meth) acryloyloxy-
 hexasiloxane 1,3,3,3-tetramethyl-1-trimethylsilyloxy-1-
 (meth) acryloyloxy-disiloxane,
 25 1-ethyl,3,3,3-trimethyl-1-trimethylsilyloxy-1-
 (meth) acryloyloxy-disiloxane,
 tris-(trimethylsilyloxy)-1-methacryloyloxy-silane and
 polymers thereof.

30 12. A process according to any preceding claim, wherein
 the catalysts are independably selected from DMF, DMSO,
 formamide, N-alkylformamides, N,N-dialkylformamides,
 acetamide, N-alkylacetamides, N,N-dialkylacetamides, N-
 Methyl pyrrolidone, p-dimethylaminobenzaldehyde, DMAP, N-
 35 methyl imidazole, 1,2-dimethyl imidazole, HMPA, DMPU,
 NaI, MeONa, MeOLi, Bu₄NF, Ph₃PO, LiOH, LiStearate and
 pyridine N-oxide.

13. A process according to any preceding claim, wherein the catalysts are present at a level of 0.001-100 mol% (mol/mol silane).
- 5 14. A process according to any preceding claim, wherein the reaction includes a polymeric inhibitor.
15. A process according to any preceding claim, wherein
10 the reaction is carried out in a suitable solvent.
16. A process according to claim 15, wherein suitable solvents include non polar inert solvents, aliphatic hydrocarbons, cyclic and non cyclic ethers.
- 15 17. A process according to any claims 15 or 16, wherein the solvent is independently selected from pentane, hexane, heptane, toluene, xylene, benzene, mesitylene, ethylbenzene, octane, decane, decahydronaphthlene, diethyl
20 ether, diisopropyl ether, diisobutyl ether or mixtures thereof.
18. A process according to any of claims 15-17, wherein
25 the solvent causes no distillation of any of the reactants but allows reactive distillation.
19. A process according to any of claims 15-18, wherein the solvent forms a low boiling azeotrope with the distilled R⁸OH.
- 30 20. A process according to any of claims 15-19, wherein the solvents are independently selected from pentane, hexane, heptane, toluene and xylene.
- 35 21. A process according to any preceding claim, wherein the reaction is carried out in the range 0°C - 200°C.

22. A process according to any preceding claim, wherein a polymerisation inhibitor is present in the range 0.001-10% wt/wt of the total reaction mix.

5 23. A process according to any preceding claim, wherein the molar ratio of silane:acid is between 1:100 and 50:1.

24. A process according to any preceding claim, wherein the solvent is at least 10 wt% of the total reaction mix
10 at the start of the reaction.

25. A hydrocarbyl silyl monomer as defined in formula I produced by a process in accordance with any of claims 1-
15 24.

26. A process according to claim 1, wherein the number of (alk)acryloyl groups in formula I is less than 4.

27. A process according to claim 1, wherein the number of
20 (alk)acryloyl groups in formula I is less than 1.

28. A process according to claim 1, wherein when R^{10} represents alkyl or hydrogen in formula II, it represents $-(SiR^4R^5O)_n-SiR^1R^2R^3$ in formula I, wherein n and R^1-R^5 are as
25 defined previously.

29. A process according to claim 1, wherein when R^1 , R^2 , R^3 , R^4 or R^5 are aryloxyl, alkaryloxyl, alkoxyl or hydroxyl in formula III, they may represent or $-O-C(O)-C(R^6)=CHR^7$ in
30 formula I.

30. A process according to claim 1, wherein where R^9 represents an alkyl group or an hydrogen atom in formula (II), it may represent $-(SiR^4R^5O)_n-SiR^1R^2R^3$ in formula (I).
35

31. A process according to any of claims 1-6 or 8-30 wherein said catalyst may be a metal alkoxide, an organic

tin compound or a boron compound or cyclic 1,3,5-triisopropoxycyclotrialuminoxane and the like.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/15003

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F7/18 C07F7/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MASAOKA, SHIGERU ET AL: "Poly'dimethylalkylsilyl (meth)acrylates!" retrieved from STN Database accession no. 108:56807 CA XP002241310 abstract	1-24, 26-31
X	& JP 62 179514 A (CHUGOKU MARINE PAINTS, LTD., JAPAN;TOSHIBA SILICONE CO., LTD.) 6 August 1987 (1987-08-06) --- -/-	25

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the International filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the International filing date but later than the priority date claimed

- "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the International search

23 March 2004

Date of mailing of the International search report

30/03/2004

Name and mailing address of the ISA
European Patent Office, P.B. 6818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rinkel, L

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 03/15003

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MASUOKA, SHIGERU ET AL: "Manufacture of polymerizable monomers of silyl esters of maleate monoesters" retrieved from STN Database accession no. 119:28788 CA XP002241311 abstract	1-24, 26-31
X	& JP 05 025186 A (NIPPON OILS & FATS CO LTD, JAPAN) 2 February 1993 (1993-02-02) -----	25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/15003

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-24,26-31

Process for the production of compounds of formula (I)

2. Claim : 25

Compounds of formula (I)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/15003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 62179514	A	06-08-1987	JP 1845361 C	25-05-1994
			JP 5056765 B	20-08-1993
JP 5025186	A	02-02-1993	NONE	